PATENT ABSTRACTS OF JAPAN

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C08L 67/03

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(71)Applicant : HITACHI CHEM CO LTD

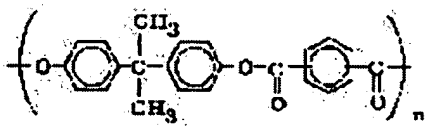
(72)Inventor : TAKAHASHI ATSUSHI
YAMAMOTO KAZUNORI
NANAUMI KEN

(54) THERMOSETTING RESIN COMPOSITION

(57)Abstract:

PURPOSE: To obtain the title compsn. excellent in heat resistance, toughness and solvent resistance by using an epoxy resin and a specific arom. polyester as the indispensable components.

CONSTITUTION: The title compsn. comprises as the indispensable components an epoxy resin (e.g., ESCN-195-6 manufactured by Sumitomo Chemical Co., Ltd.) and an arom. polyester having a chemical structure having recurring units of the formula.



LEGAL STATUS

[Date of request for examination]

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than the examiner's decision of rejection or

AN 1993:561690 CAPLUS
DN 119:161690
ED Entered STN: 16 Oct 1993
TI Heat- and solvent-resistant and tough thermosetting polymer compositions
IN Takahashi, Atsushi; Yamamoto, Kazunori; Nanaumi, Ken
PA Hitachi Chemical Co Ltd, Japan
SO Jpn. Kokai Tokkyo Koho, 4 pp.
CODEN: JKXXAF
DT Patent
LA Japanese
IC ICM C08L063-00
ICS C08L067-03
CC 37-6 (Plastics Manufacture and Processing)
FAN.CNT 1

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI JP 05051517	A2	19930302	JP 1991-212054	19910823 <--
PRAI JP 1991-212054		19910823		

CLASS

PATENT NO.	CLASS	PATENT FAMILY CLASSIFICATION CODES
JP 05051517	ICM	C08L063-00
	ICS	C08L067-03
	IPCI	C08L0063-00 [ICM,5]; C08L0067-03 [ICS,5] <--

AB Title compns. contain epoxy resins and aromatic polyesters having p-OC6H4-p-CMe2C6H4OCOC6H4CO units. Thus, ESCN 195-6 (epoxy resin) 100, U 100 (aromatic polyester) 230, and 2-ethyl-4-methylimidazole 1 part were uniformly dissolved in N-methyl-2-pyrrolidone, cast onto a glass plate, dried at 120° for 10 min, demolded, fixed, and heated at 170° for 1 h to prepare a cured polymer film, which showed tensile strength 90 MPa, modulus of elasticity 2000 MPa, elongation 9%, and glass transition temperature 290°.

ST heat resistance thermosetting polymer; solvent resistance thermosetting polymer; methylpyrrolidone resistance thermosetting polymer; toughness thermosetting polymer; epoxy resin thermosetting arom polyester

IT Chemically resistant materials
(thermosets of epoxy resins with aromatic polyesters, with heat resistance and toughness)

IT Polyesters, preparation
RL: PREP (Preparation)
(epoxy, preparation of, heat- and solvent-resistant, tough)

IT Epoxy resins, preparation
RL: PREP (Preparation)
(polyester-, preparation of, heat- and solvent-resistant, tough)

IT 150377-80-3P
RL: PREP (Preparation)
(preparation of, heat- and solvent-resistant, tough)

RN 150377-80-3 REGISTRY
ED Entered STN: 01 Oct 1993
CN 1,3-Benzenedicarboxylic acid, polymer with 1,4-benzenedicarboxylic acid, 4,4'-(1-methylethylidene)bis[phenol] and Sumiepoxy ESCN 195-6 (9CI) (CA INDEX NAME)
OTHER CA INDEX NAMES:
CN 1,4-Benzenedicarboxylic acid, polymer with 1,3-benzenedicarboxylic acid, 4,4'-(1-methylethylidene)bis[phenol] and Sumiepoxy ESCN 195-6 (9CI)
CN Phenol, 4,4'-(1-methylethylidene)bis-, polymer with 1,3-benzenedicarboxylic acid, 1,4-benzenedicarboxylic acid and Sumiepoxy ESCN 195-6 (9CI)
CN Sumiepoxy ESCN 195-6, polymer with 1,3-benzenedicarboxylic acid, 1,4-benzenedicarboxylic acid and 4,4'-(1-methylethylidene)bis[phenol] (9CI)
MF (C15 H16 O2 . C8 H6 O4 . C8 H6 O4 . Unspecified)x
CI PMS
PCT Manual component, Polyester, Polyester formed, Polyother
SR CA
LC STN Files: CA, CAPLUS

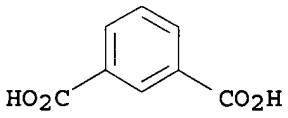
CM 1

CRN 121940-13-4
CMF Unspecified
CCI PMS, MAN

*** STRUCTURE DIAGRAM IS NOT AVAILABLE ***

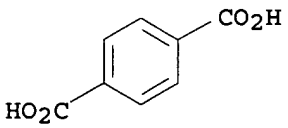
CM 2

CRN 121-91-5
CMF C8 H6 O4



CM 3

CRN 100-21-0
CMF C8 H6 O4



CM 4

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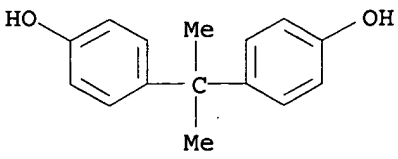


1 REFERENCES IN FILE CA (1907 TO DATE)
1 REFERENCES IN FILE CAPLUS (1907 TO DATE)

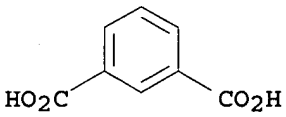
RN 26590-50-1 REGISTRY
ED Entered STN: 16 Nov 1984
CN **1,3-Benzenedicarboxylic acid, polymer with 1,4-benzenedicarboxylic acid and 4,4'-(1-methylethylidene)bis[phenol] (9CI)** (CA INDEX NAME)
OTHER CA INDEX NAMES:
CN **1,4-Benzenedicarboxylic acid, polymer with 1,3-benzenedicarboxylic acid and 4,4'-(1-methylethylidene)bis[phenol] (9CI)**
CN Isophthalic acid, polyester with 4,4'-isopropylidenediphenol and terephthalic acid (8CI)
CN **Phenol, 4,4'-(1-methylethylidene)bis-, polymer with 1,3-benzenedicarboxylic acid and 1,4-benzenedicarboxylic acid (9CI)**
CN Phenol, 4,4'-isopropylidenedi-, polyester with isophthalic acid and terephthalic acid (8CI)
CN Terephthalic acid, polyester with isophthalic acid and 4,4'-isopropylidenediphenol (8CI)
OTHER NAMES:
CN **2,2-Bis(4-hydroxyphenyl)propane-isophthalic acid-terephthalic acid copolymer**
CN **4,4'-Dihydroxydiphenylpropane-isophthalic acid-terephthalic acid copolymer**
CN **Acetic anhydride-bisphenol A-isophthalic acid-terephthalic acid copolymer**
CN Ardel 170
CN Ardel D 170
CN Ardel DM 100
CN Artrid
CN **Arylef U 100**
CN Arylef U 1060
CN **Bisphenol A-isophthalic acid-terephthalic acid copolymer**
CN **Bisphenol A-isophthalic acid-terephthalic acid polymer**
CN **Bisphenol A-terephthalic acid-isophthalic acid copolymer**
CN Delan
CN **Delan (polymer)**
CN Durel 400
CN Durel DKX 003
CN Durel DKX 008
CN DV
CN DV (polyester)
CN DV 101
CN DV 103
CN DV 105
CN DV-P
CN DV-P (polyester)
CN DV-PP
CN **Isophthalic acid-4,4'-isopropylidenediphenol-terephthalic acid polymer**
CN **Isophthalic acid-terephthalic acid-bisphenol A copolymer**
CN KL 1-9300
CN KL 1-9301
CN Poly(bisphenol A isophthalate terephthalate)
CN Poly(bisphenol A terephthalate isophthalate)
CN **Polyarylate U 100**
CN **Terephthalic acid-isophthalic acid-bisphenol A copolymer**
CN **U 100**
CN U 1060
CN U 2030
CN **U-Polymer U 100**
CN **U-Polymer U 1060**
CN **U-Polymer U 2030**
DR 59030-19-2, 132965-12-9, 76543-75-4, 150385-89-0, 155340-28-6, 106856-63-7, 111019-17-1, 203526-67-4
MF (C15 H16 O2 . C8 H6 O4 . C8 H6 O4)x
CI PMS, COM
PCT Polyester, Polyester formed

LC STN Files: AGRICOLA, BIOBUSINESS, BIOSIS, CA, CAPLUS, CASREACT, CHEMLIST, CIN, IFICDB, IFIPAT, IFIUDB, PIRA, PLASPEC*, PROMT, TOXCENTER, USPAT2, USPATFULL
(*File contains numerically searchable property data)
Other Sources: DSL**, TSCA**
(**Enter CHEMLIST File for up-to-date regulatory information)

RELATED POLYMERS AVAILABLE WITH POLYLINK

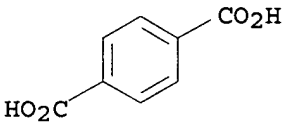
CM 1

CRN 121-91-5
CMF C8 H6 O4



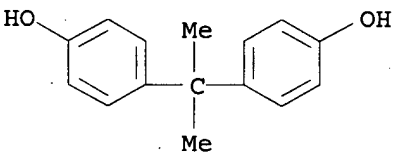
CM 2

CRN 100-21-0
CMF C8 H6 O4



CM 3

CRN 80-05-7
CMF C15 H16 O2



PROPERTY DATA AVAILABLE IN THE 'PROP' FORMAT

923 REFERENCES IN FILE CA (1907 TO DATE)
15 REFERENCES TO NON-SPECIFIC DERIVATIVES IN FILE CA
924 REFERENCES IN FILE CAPLUS (1907 TO DATE)

DERWENT-ACC-NO: 1993-112873

DERWENT-WEEK: 199314

TITLE: Thermosetting resin compsn. for use in electric and car industry - comprises epoxy! resin and aromatic polyester, having gold heat and solvent resistance

PATENT-ASSIGNEE: HITACHI CHEM CO LTD[HITB]

PRIORITY-DATA: 1991JP-0212054 (August 23, 1991)

PATENT-FAMILY:

PUB-NO	PUB-DATE	LANGUAGE	PAGES	MAINIPC
JP 05051517 A	March 2, 1993	N/A	004	C08L 063/00

APPLICATION-DATA:

PUB-NO	APPL-DESCRIPTOR	APPL-NO	APPL-DATE
JP 05051517A	N/A	1991JP0212054	August 23, 1991

INT-CL (IPC): C08L063/00, C08L067/03

ABSTRACTED-PUB-NO: JP 05051517A

BASIC-ABSTRACT:

The compsn. comprises epoxy resin and aromatic polyester having the molecular structure of formula (I).

USE/ADVANTAGE - The compsn. has good solvent resistance of epoxy resinand good heat resistance and good mechanical strength. The compsn. can be used for mouldings, films, and adhesive agents in the fields of electric, airplane and car industries. In an example, 100 pts. wt. of epoxy resin, 230 pts. wt. of aromatic polyester and 1 pt. wt. of setting catalyst (2ethyl-4-methyl imidazole) were added to 1650 pts. wt. of Nmethyl-2-pyrrolidone. The uniform soln. prepd. was placed on a glass sheet and dried at 120 deg.C under normal pressure for 10 mins. The film was parted from the glass sheet and heated at 170 deg.C for 1 hr. to give the hardened prod. of the resin compsn..

CHOSEN-DRAWING: Dwg.0/0

TITLE-TERMS: THERMOSETTING RESIN COMPOSITION ELECTRIC CAR INDUSTRIAL COMPRISE POLYEPOXIDE RESIN AROMATIC POLYESTER GOLD HEAT SOLVENT RESISTANCE

DERWENT-CLASS: A21 A81 G03

CPI-CODES: A05-A01B; A05-E10; A07-A03A; A07-A03B; G03-B02E2; G03-B02E3;

UNLINKED-DERWENT-REGISTRY-NUMBERS: 5205U; 5268U

POLYMER-MULTIPUNCH-CODES-AND-KEY-SERIALS:
Key Serials: 0016 0034 0218 0226 1282 1291 1373 1458 1460 1462 2020 2297 2302 2318 2513 2545 2600 2608 2629 2682 2737 3298 3300
Multipunch Codes: 014 02& 040 143 144 151 155 163 164 165 166 220 221 226 231 273 299 316 331 341 400 435 473 476 541 548 55& 551567 57& 609 623 627 672 721

SECONDARY-ACC-NO:
CPI Secondary Accession Numbers: C1993050143

* NOTICES *

1.This document has been translated by computer. So the translation may not reflect the original precisely.
2.**** shows the word which can not be translated.
3.In the drawings, any words are not translated.

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Industrial Application] This invention relates to the new thermosetting resin constituent which can be used for FRP used in fields, such as an electrical part, an aircraft, and an automobile, mold goods, a film, adhesives, etc. It is related with the thermosetting resin constituent which was excellent in the thermal resistance, tough nature, and solvent resistance which use an epoxy resin and aromatic polyester as an indispensable component in more detail.
[0002]
[Description of the Prior Art] The resin the advanced composite material used for an electrical part, the aircraft, etc. and for films requires high thermal resistance and the outstanding mechanical property. As resin which suits these demands, although the epoxy resin is used abundantly, generally the epoxy resin which has high thermal resistance has the fault of being weak. In order to improve the brittleness of an epoxy resin conventionally, liquid rubber is added or approaches, such as using a long-chain amide compound for a curing agent, have been taken. However, by such approach, it has the fault that thermal resistance -- the elastic modulus of a hardened material falls or glass transition temperature falls -- is unmaintainable. In order to solve this fault, the approach of mixing thermoplastics excellent in thermal resistance, such as polyether sulphone, is tried in recent years. However, by the approach of mixing thermoplastics, such as polyether sulphone, when it adds by the shape of impalpable powder to a non-hardened epoxy resin, only an uneven hardened material is obtained from generally these thermoplastics being inferior to compatibility with an epoxy resin. Moreover, even when non-hardened an epoxy resin and thermoplastics are dissolved in homogeneity with use or heating of an organic solvent, the phase separation of an epoxy resin and thermosetting resin arises after deliquoring or the hardening reaction of an epoxy resin. In these ununiformity hardened materials, we are anxious about many properties, such as solvent resistance which neither the mechanical property of an epoxy resin nor whose thermal resistance improved, and excelled [one side] in the epoxy resin, falling.
[0003]
[Problem(s) to be Solved by the Invention] This invention was made in view of this situation, and uses the thermosetting resin constituent excellent in tough nature, thermal resistance, and solvent resistance as an offer plug.
[0004]
[Means for Solving the Problem] That is, this invention is characterized by being characterized by using as an indispensable component the aromatic polyester which has specific structure, and an epoxy resin. For the aromatic polyester applied to this invention, a repeat unit is a general formula (1).
[Formula 2]

If it comes out and has the molecular structure shown, when it is molecular weight and a copolymer, it will not limit especially about the rate. Generally this compound is obtained from aromatic series dicarboxylic acid or its derivative, and dihydric phenols, such as bisphenol A, or the derivative of those, and for example, U polymer (Unitika, Sumitomo Chemical U-100) is mentioned as a concrete thing.
[0005] Moreover, as long as it is the compound which averages in the molecule and has many epoxy groups from two pieces, a limit may not have the epoxy resin applied to this invention in the molecular structure, molecular weight, etc., and it may be the aliphatic series of saturation or partial saturation, annular aliphatic series, aromatic series, or a heterocyclic compound, and may be a compound which contains functional groups, such as a halogen atom, a hydroxyl group, and a ether group, further. As an example of such an epoxy resin, bisphenol A, Bisphenol F The diglycidyl ether compound guided from halogenation bisphenols, such as dihydric phenols, such as Bisphenol S, hydroquinone, and resorcinol, or tetra-bromine bisphenol A, The novolak system epoxy resin guided from the novolak resin which is the resultant of phenols, such as a phenol and o-cresol, and formaldehyde, Para aminophenol, m-aminophenol, 4, and 4'-diamino diphenylmethane, The aromatic amine system epoxy resin guided from p-phenylene diamine, m-phenylenediamine, m-xylylene diamine, etc., The diglycidyl compound guided from aromatic carboxylic acid, such as a p-oxy-benzoic acid, an m-oxy-benzoic acid, a terephthalic acid, and isophthalic acid, a hydantoin system epoxy resin, cycloaliphatic epoxy resin or these rubber, an urethane denaturation compound, etc. are mentioned. In addition, in this invention, two or more these epoxy resins can also be used for coincidence. Moreover, the epoxy resin in this invention can be used together with compounds generally used as a curing catalyst of an epoxy resin, such as imidazole derivatives, tertiary amines, and a boron-trifluoride complex, and can be used.
[0006] In this invention, the following reasons can be considered about the thermosetting resin constituent thermal resistance and tough nature excel [constituent] in using as an indispensable component the aromatic polyester which has the specific molecular structure, and an epoxy resin being obtained. That is, the aromatic polyester and the epoxy resin which are applied to this invention are excellent in compatibility, and it is possible to obtain uniform mixture in the condition without the reaction of an epoxy resin. Moreover, as for an epoxy compound, it is well-known that it is possible to form covalent bond by ester and the addition reaction at **********, vol.49, No.3,218 (1991), etc. As mentioned above, in the mixed state without a reaction in aromatic polyester and an epoxy resin, or the hardening condition after a reaction, it can have a firm interaction between mutual molecules or between matrices, and the bridge formation mesh of an aromatic polyester molecule and a hardening epoxy resin can consider forming a very precise distributed condition. Consequently, it becomes possible to be compatible by high order origin in the thermal resistance and solvent resistance which were excellent in the epoxy resin, and the tough nature of aromatic polyester.
[0007] The compounding ratio of the aromatic polyester in this invention and an epoxy resin can be adjusted [the class of aromatic polyester or epoxy resin, and] to arbitration according to the property to need. In order to acquire especially excellent thermal resistance and tough nature, and solvent resistance, it is desirable to use the compounding ratio of aromatic polyester and an epoxy resin between 99 to 1 and 1 to 99 (weight ratio). It becomes difficult for the compounding ratio of aromatic polyester and an epoxy resin to obtain a hardened material with good solvent resistance above 99 to 1 (weight ratio). Moreover, as for tough nature, below 1 to 99 (weight ratio) is [the compounding ratio of aromatic polyester and an epoxy resin] insufficient. In addition, especially the manufacture approach of a thermosetting resin constituent and the hardening approach by this invention are not limited, and can choose the various manufacture approaches and the hardening approach according to the configuration and application. Below, an example explains this invention more concretely.
[0008]
[Example]
The example 1, example 1 of comparison, and 2 example 1 epoxy-resin (Sumitomo Chemical ESCN-195 -6) 100 weight section, the aromatic polyester (Sumitomo Chemical make U-100) 230 weight section, and the curing catalyst (2-ethyl-4-methylimidazole made from Wako Pure Chem Industry) 1 weight section were added in the N-methyl-2-pyrrolidone 1650 weight section, and the homogeneity

solution was obtained. Next, this solution was cast on the glass plate and it dried for 10 minutes by 120 degrees C and ordinary pressure. Then, after carrying out the ** form of the film-like resin mixture from the glass plate and fixing with a metal flask, heating was performed at 170 degrees C for 1 hour, and the film-like resin hardened material was obtained. About this resin hardened material, the tension test was performed at the room temperature and it asked for tensile strength, the elastic modulus, and the elongation percentage. Moreover, the dynamic viscoelasticity trial was repeated twice per same test piece with the programming rate of 5 degrees C from a room temperature to 300 degrees C, and was performed, and it asked for glass transition temperature from the temperature which shows the maximum of the loss tangent in the 2nd measurement. Furthermore, solvent resistance was searched for from the weight retention before and behind the 4-hour immersion in a N-methyl-2-pyrrolidone. A result is shown in Table 1.

[0009] It replaced with the aromatic polyester 230 weight section in example of comparison 1 example 1, and the N-methyl-2-pyrrolidone 1650 weight section, and the tension test was performed using the resin hardened material obtained by the same technique as an example 1 using the polyether sulphone (Sumitomo Chemical Victrex 4800 G) 230 weight section and the N-methyl pyrrolidone 950 weight section. Moreover, although the dynamic viscoelasticity trial was performed by the same technique as an example 1, at the time of the 1st temperature up termination, the test piece was deforming with heat, and 2nd measurement was not completed. Furthermore, solvent resistance was searched for from the weight retention before and behind the 4-hour immersion in N-methyl pyrrolidone. A result is shown in Table 1.

[0010]

[Table 1]

項目		実施例1	比較例1	比較例2
樹脂重配量合部	エポキシ樹脂	100	100	100
	芳香族ポリエステル	230	0	0
	ポリエーテルスルホン	0	230	0
	硬化触媒	1	1	1
硬化物特性	引張り強さ（MPa）	90	45	測定不可
	弾性率（MPa）	2000	2700	測定不可
	伸び率（%）	9	2	測定不可
	Tg（粘弾性法、℃）	290	210*)	測定不可
	耐溶剤性（重量保持率、%）	100	（溶解）	100

*）昇温1回目の測定値

[0011] It turns out that the resin hardened material using the thermosetting resin constituent of this invention is excellent in tough nature since tensile strength and elongation are large as compared with

the resin hardened material of the example 1 of a comparison so that an example 1 may see. Moreover, since the resin hardened material using the thermosetting resin constituent of this invention has little deformation by the temperature up of a repeat as compared with the resin hardened material of the example 1 of a comparison and glass transition temperature is high, it turns out that it excels also in thermal resistance. Furthermore, solvent resistance is also known by that it is good.
The homogeneity solution which added and obtained the example of comparison 2 epoxy-resin (Sumitomo Chemical ESCN- 195 -6) 100 weight section and the curing catalyst (2-ethyl-4-methylimidazole made from Wako Pure Chem Industry) 1 weight section in the N.N-dimethylformamide 570 weight section was cast on copper foil, and it dried by the same technique as an example 1. Heating was performed at 170 degrees C for 1 hour, copper foil was removed after that, and the resin hardened material was obtained. This resin hardened material was not able to obtain a test piece weak [very] and required to measure a property.
[0012]
[Effect of the Invention] As mentioned above, according to this invention, the thermosetting resin which has high thermal resistance and the outstanding tough nature is obtained, with the outstanding solvent resistance maintained which is the advantage of an epoxy resin so that clearly.

[Translation done.]